Lithophile Trace Element Distributions in Individual Phases from Equilibrated Ordinary Chondrites.

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We have made *in situ* ion probe analyses for 23 lithophile trace elements in phosphates, clinopyroxene (cpx), plagioclase (plag), orthopyroxene, and olivine in Guarena (H6), Marion(Iowa, L6), and St. Severin (LL6). This study has dual, but interlocking, objectives: (1) to compare directly measured crystal-crystal element ratios with expectations from laboratory crystal-liquid partitioning measurements, (2) to constrain conditions and processes accompanying ordinary chondrite metamorphism.

At temperatures relevant to ordinary chondrite metamorphism (below $1000^{o}C$) virtually no experimental constraints for crystal/crystal trace element partitioning have been established. Because such data does not exist, we adopt here the working hypothesis that trace elements are equilibrated among the co-existing phases, at least locally, defining equilibrium crystal-crystal partition coefficients. This hypothesis is subject to test from the internal systematics of the data.

Despite extended metamorphic time scales [1] type 6 chondrites are incompletely equilibrated in some respects, (e.g. textural, as shown by the presence of relict chondrules), but highly equilibrated in others, (e.g. Fe/Mg in olivine and orthopyroxene). Relatively little is known about the degree of interphase equilibration of trace elements. Our investigation also provides fundamental material balance data on many elements, as well as addressing issues of element mobility and redox conditions during chondritic metamorphism.

Experimental. Trace-element abundances were measured with PANURGE, a modified IMS 3f ion microprobe located at Caltech. A 3-10 nA, O⁻ primary beam focused to 20-30 µm was used and secondary ions were measured at low mass resolution with energy filtering. Concentrations are calculated relative to well characterized standards based on Ca-normalized count rates. Major element counting rates were monitored during individual mass scans to insure our data reflect phases free of discernible inclusions. Post-analysis SEM examination of the actual ion probe spots verified that the analyzed areas corresponded to apparently single phase regions. Major element concentrations were determined with the Caltech 733 JEOL superprobe using 15keV accelerating voltage with a 50na beam current (as measured in the Faraday cup).

Results and Discussion The data presented here refer to 1-3 grains of each phase in single regions of each meteorite, each grain separated by less than approximately 100 µm. For most elements reported here, *intergrain* variations are less than 3 sigma

counting statistics errors or less than 20% of average concentrations. Overall, our data correspond to qualitative geochemical expectations for lithophile element partitioning. The REE form the best comparison with laboratory partitioning data, as a very large number of measurements, especially for cpx, have been reported. Figure 1 compares merrillite/cpx ratios for REE with the same ratio estimated from crystal-liquid partition coefficients. Because merrillite is the dominant REE host phase, the CI-normalized REE pattern is relatively flat. Cpx, however, shows the well-established preferential affinity for the heavy REE, thus accounting for the monotonically decreasing trend in Figure 1. The similarity of the trends for the three chondrites argues that an equilibrium distribution is being measured. Crystal-crystal partition coefficient data can be inferred from D measurements only if the crystalline phases are in equilibrium with the same liquid composition at the same temperature and pressure. Such data are unavailable; consequently we have selected D(merrillite) and D(cpx) values for the closest possible compositions [2,3] with D(cpx) measured in a P-bearing liquid (but with less P_2O_5 than present in the D(merrillite) measurements). Data in [3] are only for Sm; the overall DREE pattern is form [6]. There is good agreement in the shapes of the trends. Because D(cpx) decreases with increasing liquid P content, it is likely that our adopted D(cpx) are too high, qualitatively explaining the differences in the absolute values of the trends in Figure 1.

Table 1 summarizes plag/cpx partitioning data for 5 lithophile elements. Except for Ba there is good agreement among the three chondrites. Comparison with relative plag/cpx Ds requires assumptions, and as shown in the Table, all models considered match poorly with the chondrite data.

Our phosphate and cpx REE patterns show negative Eu anomalies which, along with large positive anomalies in plag, indicate the presence of significant quantities of Eu^{2+}. If Sr partitioning is identical to Eu^{2+}, as commonly assumed, Sr/Eu ratios would be the same in all phases. Table 2 shows that this is not true. The Sr/Eu ratio drops systematically in going from plag to cpx to merrilite, showing qualitatively that Eu^{3+} is also significant. However, Sr/Eu also reflects the strong affinity of merrillite and cpx for heavy trivalent REE, making Eu^{3+} quantitatively less important than it would appear. Values for total Eu^{2+}/Eu^{3+} can be calculated from our Sr and Eu^{3+} (interpolated) crystal-crystal partition coefficients along with modal abundances. An approximate but simpler estimate can also be made by noting that the trivalent heavy REE concentrations in plag are very low, thus the plag/(merrillite+cpx) mass

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balance ratio for Eu is a lower limit (but approximately equal) to the total Eu^{2+}/Eu^{3+}. For St. Severin, for which accurate modes are available [3] we estimate $Eu^{2+}/Eu^{3+} = 2.5$.

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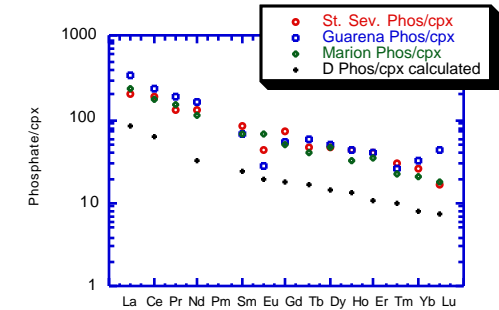
Figure 1. Measured effective D values for the 3 meteorites investigated. For comparison, calculated D values derived from experiment [3,6] are plotted (+ symbols). Qualitative agreement is good, but additional measurements/experimental data are needed for quantitative comparison.

Table 1. Plag/cpx partitioning.

	Sr	Ba	La	Ce
Guarena (H6)	12.8	52.6	0.234	0.0472
Marion (L6)	13	184	0.277	0.0441
St. Sev. (LL6)	14.5	84	0.192	0.0371

From D(plag)/D(cpx)

Model IA	10	59	0.71	0.31
Model IB	18	106	1.26	0.55
Model IC	19		0.48	0.125
Model II1.8	336	0.033	0.014	

Models:
A major problem is the lack of plag/cpx crystal/liquid partitioning data for Na-rich plagioclase, as found in equilibrated chondrites. Model 1 adopts D (plag) from (4; composition 6) and various choices of D (cpx): A. Using the D_{Ca} correlation of (5; figure 5) for the liquid CaO of [4] and the DREE (cpx) pattern of [6]; B. Using the D_{Ho} (cpx)-SiO_2 liquid correlation of [7], the DREE (cpx) pattern of [6], and the SiO_2 liquid of (4, composition 6); C. Using Dcpx from [8]. Model II uses the D model of [9] normalized to D_{Na} (plag) and Dca (cpx) for the AbDi eutectic composition.

Table 2.

Sr/Eu.	Guarena	St. Sev.	Marion
plag	182	193	153
cpx	87	93	131
merrillite	20	8.8	21